Decreases in upper atmospheric chlorine

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Abstract

We report a steady decrease in the global upper stratospheric and lower mesospheric abundances of hydrogen chloride (HCl) from August, 2004, through January, 2006, as measured by the Microwave Limb Sounder (MLS) aboard the Aura satellite. The average yearly change in the 0.7 to 0.1 hPa region is –27 ± 3 pptv/year, or –0.78 ± 0.08 percent/year. This is consistent with surface abundance decrease rates (about 6 to 7 years earlier) in chlorine source gases. The MLS data confirm that international agreements to reduce global emissions of ozone-depleting industrial gases are leading to global decreases in the total gaseous chlorine burden. Tracking stratospheric HCl variations on a seasonal basis is now possible with MLS data. Inferred stratospheric total chlorine (Cl_{TOT}) has a value of 3.60 ppbv at the beginning of 2006, with a (2-sigma) accuracy estimate of 7%; the stratospheric chlorine loading has decreased by about 43 pptv in the 18-month period studied here. We discuss the MLS HCl measurements in the context of other satellite-based HCl data, as well as expectations from surface chlorine data. A mean age of air of ~ 5.5 years and an age spectrum width of 2 years or less appear to best fit the ensemble of measurements.

1. Introduction

The abundances of chlorine and bromine gases in the Earth's stratosphere have garnered much attention in ozone depletion assessments [e.g., *WMO*, 2003], because of the consensus regarding the importance of industrially-produced source gases such as chlorofluorocarbons (CFCs) and halons. Measurements from surface networks, as well as from aircraft, have produced a record of chlorine gases and their total abundance

(Cl_{TOT}) in the troposphere for more than two decades. Also, ground-based column measurements of (largely stratospheric) hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$), as well as satellite-based near-global observations of HCl at high altitude (near 55 km), have documented the long-term increase in total stratospheric chlorine up until the late 1990s, with indications of a turn-around in recent years [*Anderson et al.*, 2000; *WMO*, 2003]. The vast majority of chlorine in the upper stratosphere and lower mesosphere is present as HCl, as shown by early observations from the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment [*Zander et al.*, 1996], and recently corroborated by data from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS, often simply referred to as ACE, below) aboard the Canadian satellite SCISAT-1 [*Bernath et al.*, 2005].

Here, we report and analyze recent decreases in upper atmospheric HCl, observed by the Microwave Limb Sounder (MLS) aboard the Aura satellite, launched July 15, 2004. These results are discussed in the context of other HCl measurements, including those from ACE and the 14-year record from the Halogen Occultation Experiment (HALOE) [*Russell et al.*, 1993] on the Upper Atmosphere Research Satellite (UARS). We discuss the implications of the various results in terms of stratospheric total chlorine and decreases expected from tropospheric chlorine data.

2. Variations in tropospheric chlorine and upper atmospheric MLS HCl data

Figure 1 shows the tropospheric chlorine abundance based on surface measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE) network [e.g., *O'Doherty et al.*, 2004], and from the National Oceanic and Atmospheric

Administration (NOAA) network [*Montzka et al., 1999*]. We have averaged these two datasets to produce a mean estimate of total chlorine in the troposphere; differences between the two networks are less than 30 ppt (1%) over the time period of overlap. This chlorine loading peaked in late 1993 to early 1994 at close to 3.7 ppb (the peak combined value from Figure 1 is 3.692 ppb). Peak tropospheric Cl_{TOT} should represent an upper limit for stratospheric Cl_{TOT}, where the peak is expected a number of years later. The total chlorine abundances in Figure 1 include 100 ppt from the chlorinated very short-lived (VSL) gases CH_2Cl_2, $CHCl_3$, C_2Cl_4, and $COCl_2$. We note that for long-lived source gas measurements, the root sum square difference between the two networks is ~23 ppt of Cl, or 0.6%. This becomes 1.5% if one adds (in root sum square fashion) 50 ppt uncertainty in Cl from VSL compounds. An accuracy estimate of about 2% therefore seems to represent the current state of knowledge for the total tropospheric chlorine burden.

The Earth Observing System (EOS) MLS is one of 4 instruments aboard Aura, and MLS measures thermal emission from the limb in five spectrally-broad regions [*Waters et al.,* 2006]. HCl emission lines near 625 GHz are used to retrieve ~3500 HCl profiles daily (day and night) with ~165 km spacing along the 82°S to 82°N sub-orbital track. Vertical resolution for HCl data (version 1.51) is ~3-4 km in the lower stratosphere and 6 km in the upper stratosphere. The MLS retrievals [*Livesey et al.,* 2006] use a linearly-connected set of coefficients on a 6-point per decade pressure grid and account for horizontal variations along the sub-orbital track. MLS sensitivity to HCl is evident in the MLS radiance data as high as the upper mesosphere. Early comparisons

of HCl from MLS with other satellite and balloon data are described by *Froidevaux et al.* [2006], with further discussion in section 3.

Figure 2 shows that MLS has measured a decrease in HCl abundances in the upper stratosphere and lower mesosphere between August 2004 and January 2006. The MLS measurement density, repeatability, and precision allow global HCl decreases on a seasonal basis to be precisely tracked (within a given year) for the first time. The average yearly decrease, based on an average of the first 6 months and the last 6 months of these time series, amounts to about 27 pptv (with a scatter from the various altitudes of 3 pptv), or a slope of –0.78 %/yr (and scatter of 0.08 %/yr). The HCl changes shown in Figure 2 are well outside the typical precision in the monthly means; for example, the 2-sigma uncertainty at 0.46 hPa (~53 km) is under 0.003 ppbv, which is one twentieth of the total change. Tropospheric chlorine variations, with a time lag, should govern the overall temporal changes in upper stratospheric and lower mesospheric total chlorine, although some non-linear effects due to mixing can occur [e.g., *Waugh et al.*, 2001]. A calculation of decrease/year as performed for the MLS HCl data, but based on tropospheric chlorine variations time-lagged by 7 years and multiplied by 0.96 to account for the ratio HCl/Cl_{TOT}, gives 29 pptv/year, in very good agreement with MLS data. The factor of 0.96 is based on the 2-D Simulation of Chemistry, Radiation, and Transport of Environmentally important Species (SOCRATES) model results shown in Figure 3, as well as recent evidence from an ACE-FTS inventory of chlorine species in the stratosphere [*Nassar et al.*, 2006], indicating possibly slightly larger values of HCl/Cl_{TOT} in the upper stratosphere. Peak values of HCl/Cl_{TOT} shown in Figure 3 are between 0.95 and 0.96; additional model chlorine above 55 km comes mainly from ClO and Cl (~ 3%

of total), from the $CHClF_2$ (HCFC-22) long-lived organic contribution (~ 1%), and HOCl (0.5%). A time lag of 6 years also leads to reasonable agreement between the MLS data in Figure 2 and expectation, the ground-based decrease (6 years earlier) being ~27 pptv/year. However, a lag under 5 years produces a decrease of under 20 pptv/year, which is less consistent with the MLS data. The smaller decrease (for shorter time lags) occurs because the rate of decline of tropospheric chlorine has slowed in recent years, mainly as a result of the rapid but (now) slowing decline in CH_3CCl_3 [*Montzka et al.*, 1999; *O'Doherty et al.*, 2004]. More complex (and probably more robust) considerations of time lags involve mean age (transport timescale) of air and spectral widths of the age distribution for a mixture of air parcels; this is discussed in section 3.

Figure 4 shows global upper atmospheric averages of MLS HCl and inferred values of Cl_{TOT} versus height, with the conversion of HCl to Cl_{TOT} based on an integration of SOCRATES 2-D model HCl/Cl_{TOT} values in ten degree latitude bins. The differences between August 2004 and January 2006 show that the temporal decrease has occurred at all heights in this region. Cl_{TOT} (averaged over the various pressures) has changed from 3646 to 3603 pptv in this 18-month period, for an average decrease of 43 pptv ± 9 pptv (precision in the mean). Cl_{TOT} is fairly constant with height, meaning that model and MLS HCl dependences on height are quite similar; the Cl_{TOT} values near the peak are less sensitive to the model profile shape. At the highest altitudes, both MLS and model values show a small decrease attributed to photolysis of HCl. The 2-sigma accuracy estimate for MLS HCl is ~ 5%, based on a consideration of the various possible error sources, to be discussed in a future validation paper; uncertainties arising from HCl linewidth parameters for upper stratospheric temperatures are ~ 3 % [*Drouin et al.*, 2004]

and account for more than half of the accuracy value. The estimated accuracy for inferred Cl_{TOT} is 7%, obtained by (conservatively) adding 2% uncertainty from HCl/Cl_{TOT}.

3. Other Results and Discussion

To place the MLS measurements in the context of other satellite datasets for HCl, Figure 5 shows the MLS monthly mean HCl time series at 0.46 hPa for 60°S – 60°N, similarly-averaged HALOE (version 19) monthly means (interpolated to 0.46 hPa), and ACE (version 2.2) data at 53.5 km (~ 0.49 hPa) averaged in nine 3-month periods (quarterly, from January, 2004, through March, 2006). We also show version 3 data [*Irion et al.*, 2002] from the 4 ATMOS missions, using HCl retrieval averages from 50 to 60 km in the above latitude range; the ATMOS data contain the fewest profiles and averaging over height helps to reduce the noise to below the accuracy estimate. ACE HCl values in the upper stratosphere are, on average, a few to 5% larger than MLS data, and are larger than HALOE HCl by 10-15% or more; however, ACE HCl in the lower mesosphere departs more from (and is progressively larger than) MLS HCl, as altitude increases [*Froidevaux et al.*, 2006; *Nassar et al.*, 2006]. Future work will help confirm whether (and by how much) ACE HCl values should be lowered in the mesosphere. The average ACE HCl abundance (near 53 km) from Figure 5 is 3.69 ppbv, with (1-sigma) variability of ~0.2 ppbv. However, ACE provides a mean 2004 Cl_{TOT} estimate at lower altitudes of ~3.65 ppbv [*Nassar et al.*, 2006], which is more consistent with the MLS measurements of HCl above 50 km, and in excellent agreement with the August 2004 MLS Cl_{TOT} estimate (also 3.65 ppbv, from Figure 4). We use a 2-sigma accuracy for ACE HCl of 0.3 ppbv, which is slightly larger than the estimate (0.26 ppbv) provided by

Nassar et al. [2006] for midlatitude HCl at 50 km. The value of 0.3 ppbv as an error bar (2-sigma) is used in Figure 5 for ATMOS data as well, consistent with ATMOS HCl error estimates described in the past [e.g., *Zander et al.*, 1996]. One could draw an HCl time series that is consistent with all the Figure 5 results within their above-stated uncertainties (including the HALOE accuracy value of 13%); this would require an upward adjustment of the HALOE values and a downward adjustment of the ATMOS, ACE, and (probably) MLS data by varying amounts.

In Figure 5, the HCl datasets are compared to expectations of long-term variations in HCl, as obtained from tropospheric chlorine estimates and considerations of mean age of air and various age spectrum widths [e.g., *Waugh and Hall*, 2002] relating to transport timescales and irreversible mixing of air parcels moving from the surface to the upper stratosphere. The tropospheric chlorine burden is based on total chlorine loading from Figure 1 as well as an example for the WMO 2002 Ab scenario [*WMO*, 2003], which peaks at 3.58 ppbv instead of 3.69 ppbv, because it only includes contributions from the 12 most abundant long-lived halocarbons. If very-short-lived (VSL) compounds are transported across the tropopause, it is likely that their decomposition products will contribute to upper stratospheric Cl_{TOT}. However, questions remain regarding how much chlorine can reach the lower stratosphere, either by cross-tropopause transport of the VSL species or of their decomposition products [*WMO*, 2003]. The satellite results do not place strong constraints on possible chlorine contributions from VSL gases, because of the absolute uncertainties in the measurements and differences between the datasets. While HALOE data are most consistent with no chlorine contribution from VSL compounds, the MLS, ACE, and ATMOS data suggest a significant contribution.

Multi-year balloon-borne observations of stratospheric tracers such as CO_2 and SF_6 have led to a mean age estimate of about 5.5 years in the middle stratosphere [*Schmidt and Khedim*, 1991; *Engel et al.*, 2002], although this is not constrained to better than ~1 year, nor is mean age necessarily constant in time. Age of air is probably roughly constant in the upper stratosphere and above, given that these and other balloon CO_2 measurements exhibit very weak vertical gradients above 25-30 km. The MLS data alone cannot distinguish between the mean ages of 5.5 or 7 years, shown as examples in Figure 5, although closer agreement with the data is obtained for a 7 year mean age. While a better constraint on mean age could in principle be obtained from HCl data during the phase of rising chlorine, the error bars and differences between datasets preclude a useful constraint. The ATMOS data would be more consistent with a mean age of 4 to 5 years, while HALOE data favor a value larger than ~5.5 years. A mean age of ~5.5 years (consistent with results from balloon-borne data) can be viewed as a consensus that might best accommodate the ensemble of datasets, within their uncertainties. In terms of the width of the age spectrum, the decrease implied by MLS data to date favors a width of 2 years or less.

HALOE data since 2000 show a steeper decrease than MLS and the various model curves, and explaining some of the variations obtained by HALOE has proved difficult [*Waugh et al.*, 2001]. In this respect, the scatter in MLS monthly means using a subset of data with a sampling that mimics the HALOE occultation data coverage was found to be smaller than the scatter in HALOE means, but larger than using the full MLS sampling. ACE seasonal averages in Figures 5 also show more variability than the MLS data, while not being inconsistent with expected decreases. Also, the HALOE data

appear to vary coherently over at least a 5 to 6 km range (for altitudes near those used and shown here). This range corresponds to the vertical resolution of MLS in that region; the coarser MLS resolution should therefore not significantly mask variations such as those exhibited in the HALOE dataset. Thus, poorer (and less repeatable) sampling in the occultation datasets is partly responsible for explaining the larger variability, even if that is not the only factor.

The MLS upper atmospheric HCl measurements to date imply that international agreements to reduce global emissions of ozone-depleting industrial gases are leading to global decreases in stratospheric chlorine, consistent with the observed decrease in surface chlorine burden. Several more years of data will better constrain our knowledge of stratospheric age of air spectrum width and transport-related variability.

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Figure 1. Tropospheric total chlorine based on source gas network data at the Earth's surface from AGAGE (green) and NOAA (blue). An average curve based on the overlap time period is shown in red. Insert gives the (ppt) difference (NOAA - AGAGE).

Figure 2. Monthly-averaged MLS HCl zonal means (curves with dots) over 60°S to 60°N for Aug. 2004 through Jan. 2006, at 6 upper atmospheric pressures, as indicated by colored labels. Dashed black lines show the uncertainty due to imprecision at 0.46 hPa, defined here as ± twice the standard error in the mean. Purple curve is upper atmospheric HCl expected from tropospheric chlorine loading (average from Figure 1), time-shifted by 7 years and adjusted by 0.96 for the HCl/Cl_{TOT} ratio (near 0.46 hPa).

Figure 3. Upper stratospheric and lower mesospheric HCl/Cl_{TOT} ratios based on recent NCAR SOCRATES 2-D model results at various northern latitudes (see legend). Values correspond to steady-state averages (3-year integration), after a model spin-up of seven years. Similar values are obtained for southern latitudes (not shown).

Figure 4. Global average upper stratospheric and lower mesospheric MLS HCl (dots) and inferred Cl_{TOT} (triangles) for August 2004 (red) and January 2006 (black). Cl_{TOT} is inferred using SOCRATES 2-D model results for HCl/Cl_{TOT} (see Figure 3). These results are based on zonal means in 10 degree latitude bins, weighted by (cosine of) latitude.

Figure 5. Top panel: Solid (blue) curve shows total chlorine (Cl_{TOT}) time series based on tropospheric data (Figure 1). Dashed curve does not include contributions from short-lived chlorinated substances (WMO 2002 scenario Ab). Middle and bottom panels: HCl data are shown as 60S-60N monthly averages at 0.46 hPa (~ 53 km) for MLS (red dots), similar averages for HALOE (purple circles), along with quarterly averages (at ~ 53 km) from ACE (in green) and ATMOS version 3 data averages (cyan squares) for 50-60 km;

see text for more discussion of data and error bars (2-sigma estimates of accuracy). Solid curves use total chlorine (top panel's solid curve) and different mean age assumptions (5.5 or 7 yr), with various age spectrum widths, as indicated; a factor of 0.96 is applied to get HCl. The dashed black curves give expected HCl based on the WMO 2002 scenario Ab and a mean age (5.5 or 7 yr) and width (2 yr) appropriate for the solid black curves.

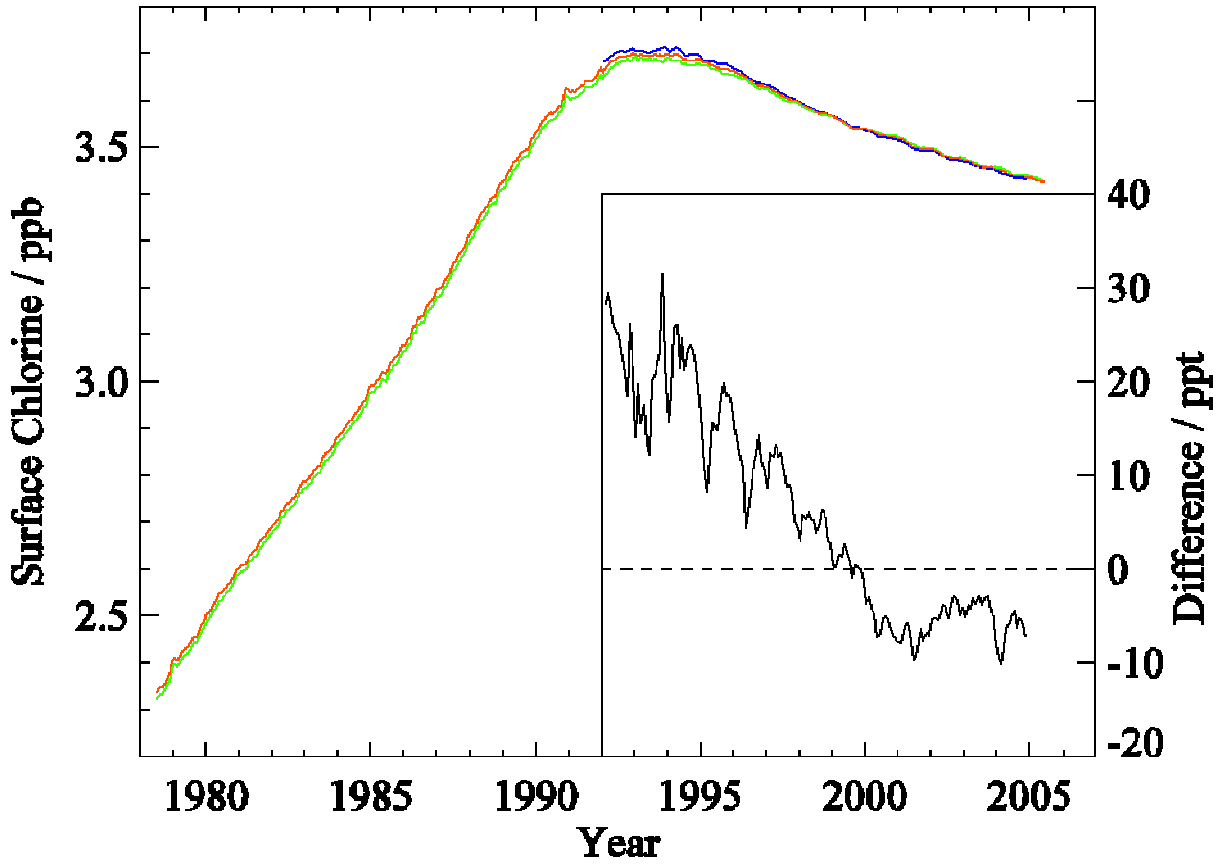
Surface Chlorine / ppb
3.5
3.0
2.5
1980
1985
1990
1995
2000
2005
Year
40
30
20
10
0
-10
-20
Difference / ppt

Figure 1.

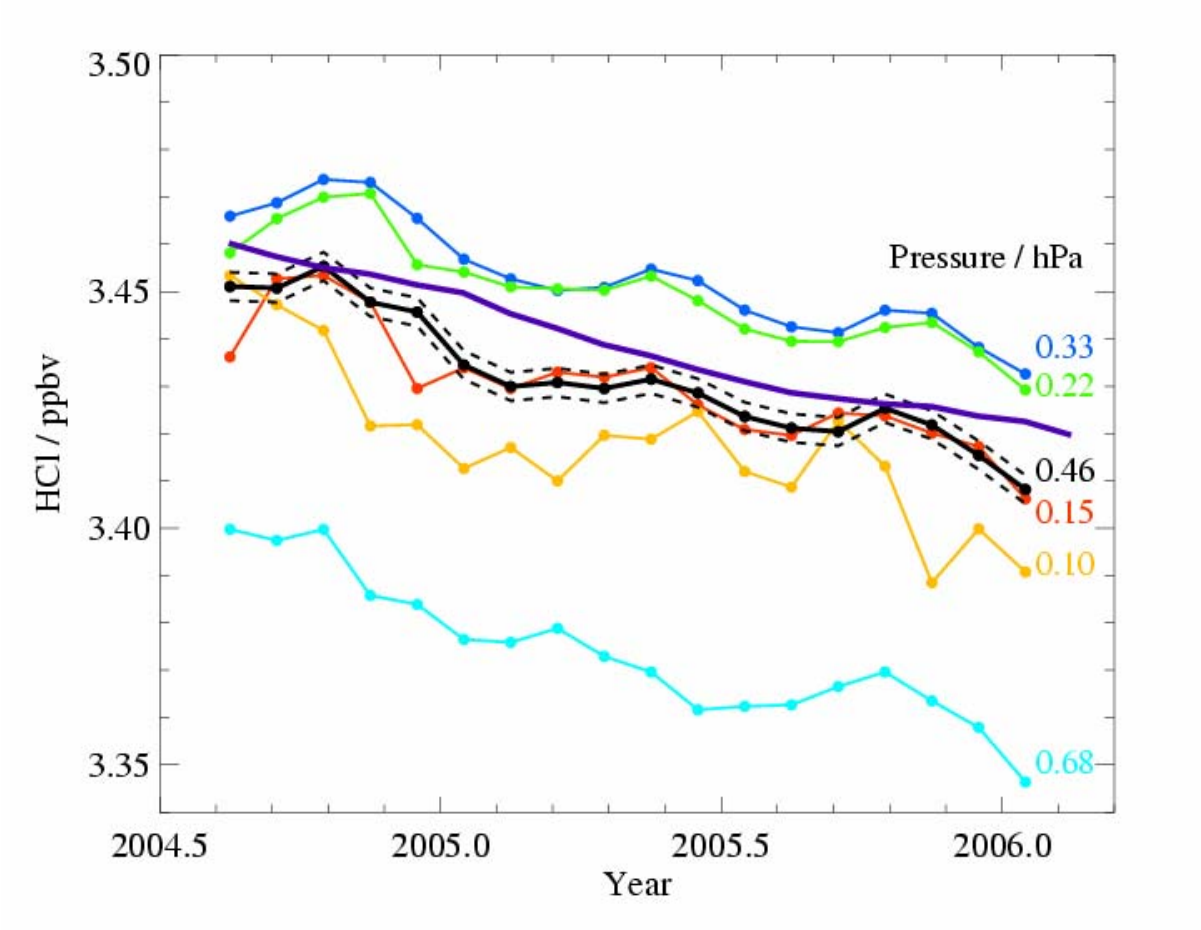
3.50
3.45
3.40
3.35
HCl / ppbv
2004.5
2005.0
2005.5
2006.0
Year
Pressure / hPa
0.33
0.22
0.46
0.15
0.10
0.68

Figure 2.

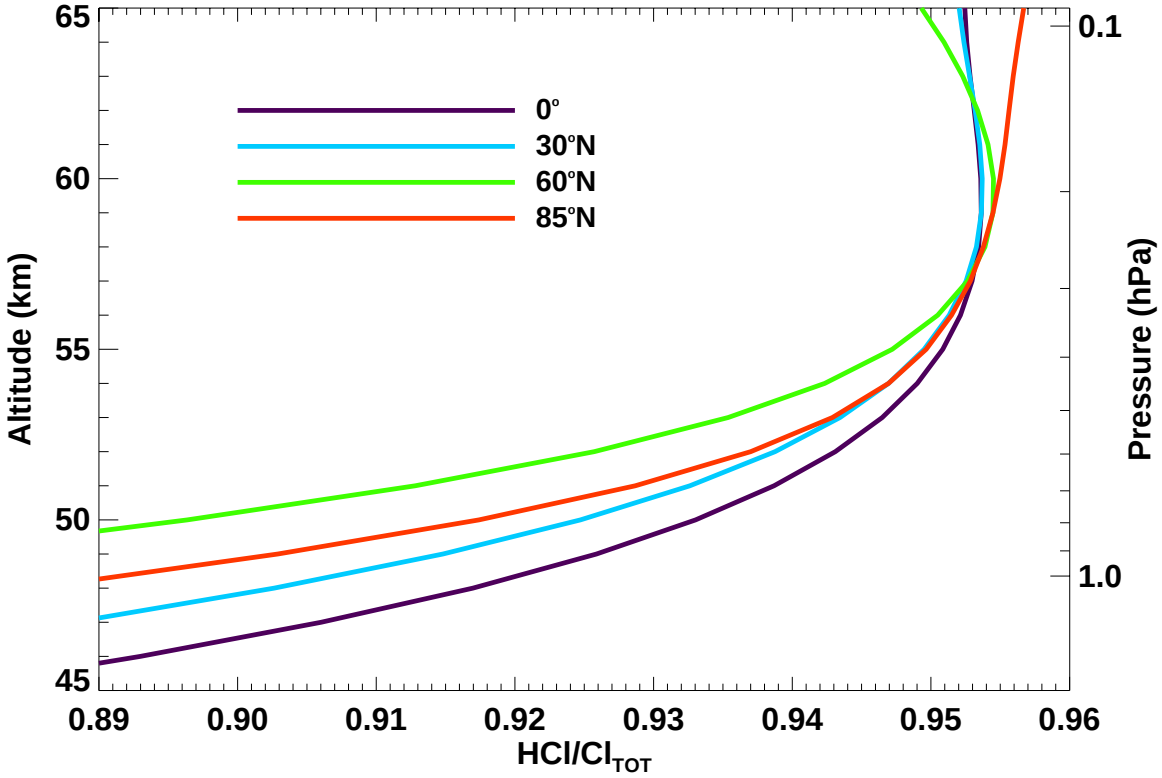
65
60
55
50
45
Altitude (km)
0.89
0.90
0.91
0.92
0.93
0.94
0.95
0.96
HCl/Cl$_{TOT}$
0.1
1.0
Pressure (hPa)
0°
30°N
60°N
85°N

Figure 3.

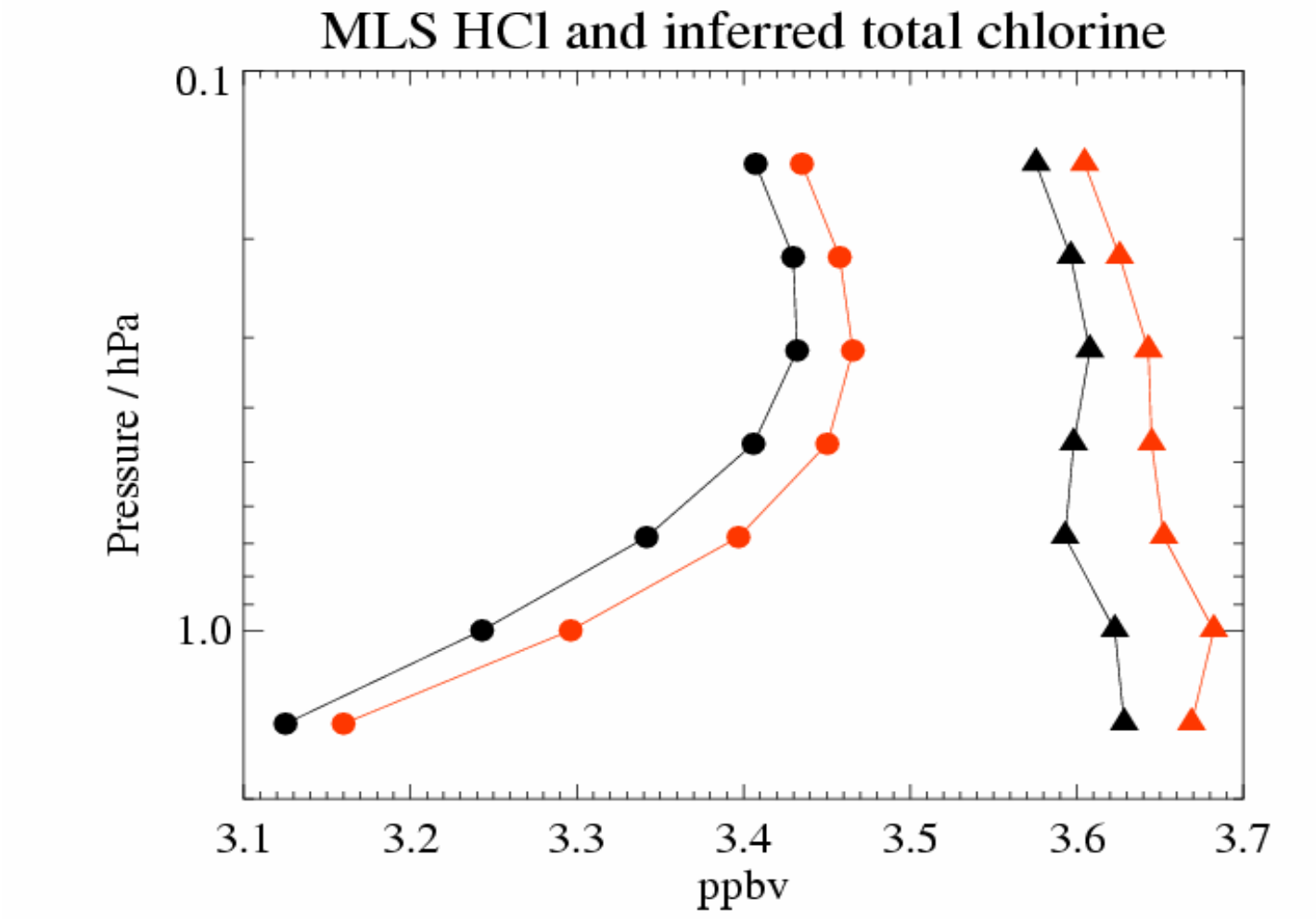
MLS HCl and inferred total chlorine
0.1
1.0
Pressure / hPa
3.1
3.2
3.3
3.4
3.5
3.6
3.7
ppbv

Figure 4.

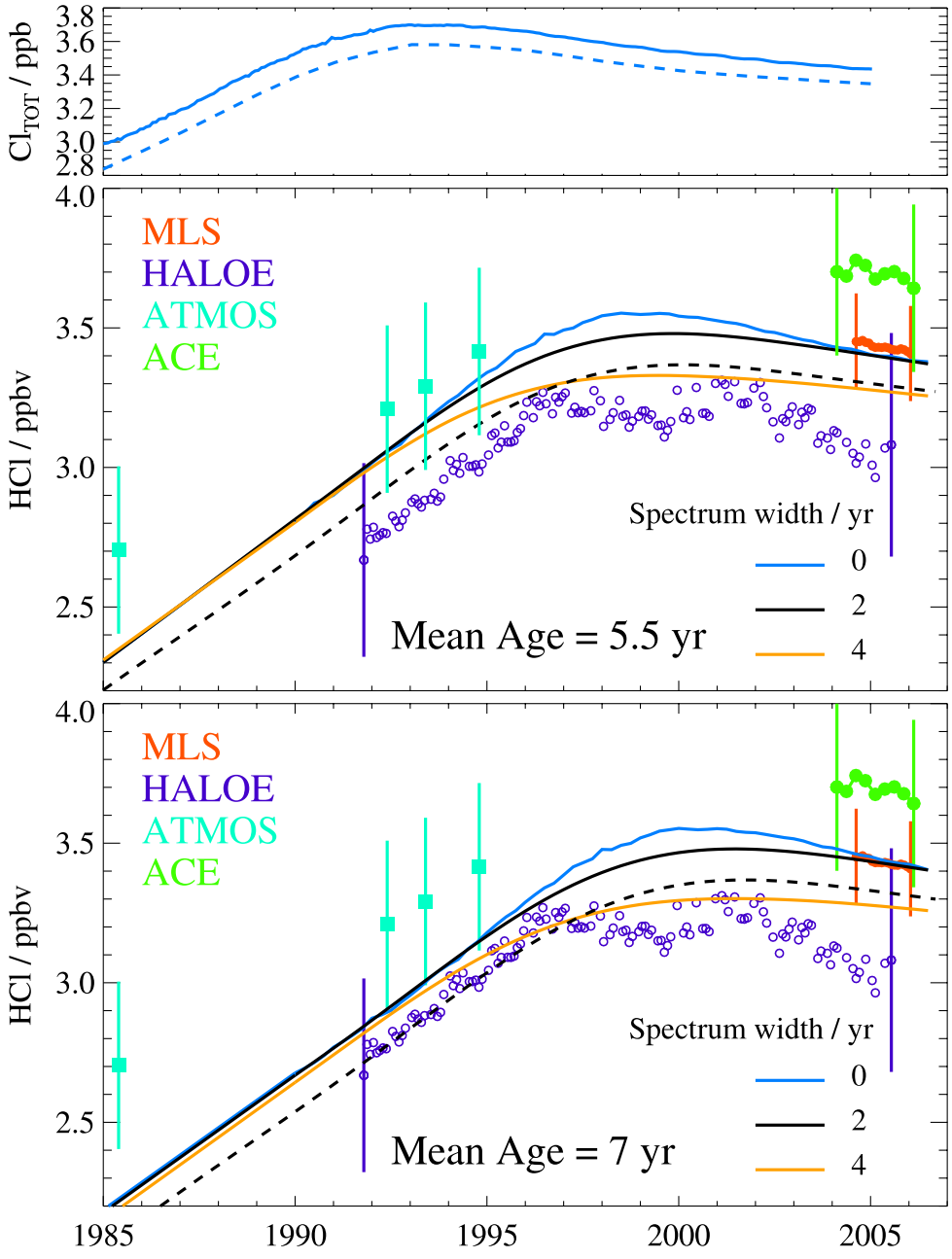
Cl_{TOT} / ppb
3.8
3.6
3.4
3.2
3.0
2.8
HCl / ppbv
4.0
3.5
3.0
2.5
MLS
HALOE
ATMOS
ACE
Spectrum width / yr
0
2
4
Mean Age = 5.5 yr
Mean Age = 7 yr
1985
1990
1995
2000
2005

Figure 5.